

CLAIMS

We claim:

1. A removable, water-whitening resistant pressure sensitive adhesive comprising a crosslinked aqueous emulsion polymer comprising:
 - 5 (a) at least one hydrophobic monomer selected from an alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, or a mixture of at least one styrenic monomer and at least one alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, wherein when a styrenic monomer is present, said styrenic monomer is present in an amount up to about 30 wt. % of the total hydrophobic monomer mixture;
 - (b) greater than 1 wt. % of at least one hydrophilic monomer;
 - 15 (c) greater than 3 wt. % of at least one mono-olefinically unsaturated monomer having an aldehyde or ketone group;
 - (d) optionally at least one partially hydrophilic monomer selected from alkyl (meth)acrylate esters of an alcohol wherein the alkyl portion of the alcohol has 1 to 2 carbon atoms, N-vinyl-2-pyrrolidone, or mixtures thereof; and
 - 20 (e) an effective amount of at least one water-soluble or water-dispersible polymerizable surfactant selected from compounds having a terminal allyl amine moiety, substituted phenyl compounds having at least one alkenyl substituent, polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salts, or mixtures thereof;
- 25 wherein said crosslinked aqueous emulsion polymer is crosslinked with at least one polyhydrazide crosslinker, the wt. % of monomers (a), (b), (c) and (d) are based on the total weight of monomers (a), (b), (c) and (d), and the mean particle size of said crosslinked aqueous emulsion polymer is less than about 400 nm.
- 30

2. The composition of claim 1 wherein the amount of monomer (a) in said crosslinked aqueous emulsion polymer is about 50 to about 95 wt. %.
3. The composition of claim 2 wherein the amount of monomer (a) in said crosslinked aqueous emulsion polymer is about 70 to about 90 wt. %.
- 5 4. The composition of claim 1 wherein the amount of monomer (b) in said crosslinked aqueous emulsion polymer is about 2 to about 10 wt. %.
5. The composition of claim 4 wherein the amount of monomer (b) in said crosslinked aqueous emulsion polymer is about 3 to about 8 wt. %.
6. The composition of claim 1 wherein the amount of monomer (c) in
10 said crosslinked aqueous emulsion polymer is about 3.5 to about 20 wt. %.
7. The composition of claim 1 wherein the amount of monomer (d) in said crosslinked aqueous emulsion polymer is 0 to about 45 wt. %.
8. The composition of claim 7 wherein the amount of monomer (d) in said crosslinked aqueous emulsion polymer is about 5 to about 25 wt. %.
- 15 9. The composition of claim 1 wherein the pH of said aqueous emulsion polymer is at least 6.
10. The composition of claim 9 wherein the pH of said aqueous emulsion polymer is about 6.5 to about 9.
11. The composition of claim 1 further comprising a non-polymerizable
20 surfactant.
12. The composition of claim 11 wherein said non-polymerizable surfactant is an ionic surfactant.
13. The composition of claim 1 wherein said removable, water-whitening resistant pressure sensitive adhesive has a peel strength of less than about 2.5 pounds
25 per inch peel force with adhesive failure mode.
14. The composition of claim 1 wherein said monomer (a) is selected from

isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, isononyl acrylate, isodecyl acrylate, or mixtures thereof.

15. The composition of claim 14 wherein said monomer (a) is selected from n-butyl acrylate, 2-ethylhexyl acrylate, or mixtures thereof.

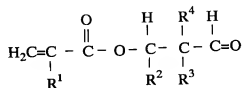
16. The composition of claim 1 wherein said monomer (b) is selected from a monoolefinic monocarboxylic acid, a monoolefinic dicarboxylic acid,

2-hydroxyethyl acrylate, or mixtures thereof.

17. The composition of claim 16 wherein said monomer (b) is selected from acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid, crotonic acid, 2-hydroxyethyl acrylate, or mixtures thereof.

18. The composition of claim 17 wherein said monomer (b) is selected from acrylic acid, 2-hydroxyethyl acrylate, or mixtures thereof.

19. The composition of claim 1 wherein said monomer (c) is selected from acrolein, methacrolein, vinylbenzaldehyde, crotonaldehyde, (meth)acryloxyalkylpropanals represented by the formula



where R¹ is -H or -CH₃, R² is -H or alkyl of 1 to 3 carbon atoms, R³ is alkyl of 1 to 3 carbon atoms, and R⁴ is alkyl of 1 to 4 carbon atoms, vinyl acetoacetate, allyl acetoacetate, vinyl methyl ketone, vinylbenzene methyl ketone, acetoacetoxyethyl methacrylate, vinyl ethyl ketone, vinyl isobutyl ketone, vinyl butyl ketone, diacetone (meth)acrylamide, diacetone (meth)acrylate, acetonyl acrylate, 2-hydroxypropyl acrylate-acetyl acetate, 1,4-butanediol acrylate-acetyl acetate, or mixtures thereof.

20. The composition of claim 19 wherein said monomer (c) is selected from diacetone acrylamide, diacetone acrylate, acrolein, or mixtures thereof.

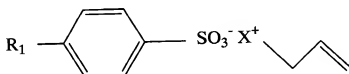
21. The composition of claim 1 wherein said monomer (d) is selected from methyl acrylate, methyl methacrylate, ethyl acrylate, or mixtures thereof.

5 22. The composition of claim 21 wherein said monomer (d) is selected from methyl acrylate, ethyl acrylate, or mixtures thereof.

23. The composition of claim 1 wherein said polymerizable surfactant has a hydrophilic portion selected from a sulfonate allyl amine moiety, a sulfate allyl amine moiety, or a phosphate allyl amine moiety, and a hydrophobic portion selected
10 from -R, or a group having the formula $\text{RO}-(\text{CH}_2\text{CH}_2\text{O})_n-$; wherein R is an alkyl group or an alkyl-substituted phenyl group wherein the alkyl group has 1 to 20 carbon atoms, and n is an integer from 2 to 100.

24. The composition of claim 23 wherein n is an integer from 2 to 15.

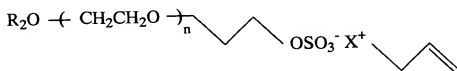
25. The composition of claim 1 wherein said polymerizable surfactant is
15 an allyl amine salt of an alkyl benzene sulfonate having the formula



wherein R_1 is an alkyl group having 1 to 20 carbon atoms, and X^+ is selected from $^+\text{NH}_3$, $^+\text{NH}_2\text{R}_4$, or $^+\text{NHR}_4\text{R}_5$, wherein R_4 and R_5 are independently selected from C_1 - C_4 alkyl or hydroxyalkyl groups.

20 26. The composition of claim 25 wherein said polymerizable surfactant is an allyl amine salt of dodecylbenzene sulfonate.

27. The composition of claim 1 wherein said polymerizable surfactant is an allyl amine salt of an alkyl ether sulfate having the formula

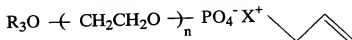


wherein R_2 is an alkyl group having 1 to 20 carbon atoms, n is an integer from 2 to 100, and X^+ is selected from $^+NH_3$, $^+NH_2R_4$, or $^+NHR_4R_5$, wherein R_4 and R_5 are independently selected from C_1 - C_4 alkyl or hydroxyalkyl groups.

28. The composition of claim 27 wherein n is an integer from 2 to 15.

29. The composition of claim 28 wherein said polymerizable surfactant is an allyl amine salt of laureth sulfate.

30. The composition of claim 1 wherein said polymerizable surfactant is an allyl amine salt of a phosphate ester having the formula



wherein R_3 is an alkyl or alkyl-substituted phenyl group wherein the alkyl group has 1 to 20 carbon atoms, n is an integer from 2 to 100, and X^+ is selected from $^+NH_3$, $^+NH_2R_4$, or $^+NHR_4R_5$, wherein R_4 and R_5 are independently selected from C_1 - C_4 alkyl or hydroxyalkyl groups.

31. The composition of claim 30 wherein n is an integer from 2 to 15.

32. The composition of claim 31 wherein said polymerizable surfactant is an allyl amine salt of nonylphenol ethoxylate (9 moles EO) phosphate ester.

33. The composition of claim 1 wherein said polymerizable surfactant is an allyl amine salt of a sulfate having the formula

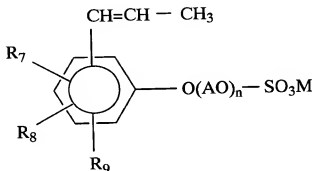


wherein R_6 is an alkyl group having 6 to 20 carbon atoms, and X^+ is selected from $^+NH_3$, $^+NH_2R_4$, or $^+NHR_4R_5$, wherein R_4 and R_5 are

independently selected from C₁-C₄ alkyl or hydroxyalkyl groups.

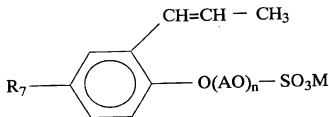
34. The composition of claim 33 wherein R₆ is an alkyl group having 10 to 18 carbon atoms.

35. The composition of claim 1 wherein said polymerizable surfactant is a substituted phenyl compound having the formula



wherein R₇ is an alkyl, alkenyl or aralkyl group containing 6 to 18 carbon atoms; R₈ is a hydrogen atom or an alkyl, alkenyl or aralkyl group containing 6 to 18 carbon atoms; R₉ is a hydrogen atom or a propenyl group; A is an unsubstituted or substituted alkylene group containing 2 to 4 carbon atoms; n is an integer of 1 to about 200; and M is an alkali metal, an ammonium ion, or an alkanolamine residue.

36. The composition of claim 35 wherein said polymerizable surfactant is a substituted phenyl compound having the formula

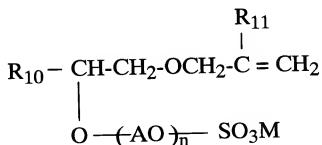


37. The composition of claim 36 wherein R₇ is alkyl, A is ethylene, and M is alkali metal or ammonium.

38. The composition of claim 37 wherein R₇ is nonyl, n is about 10 to

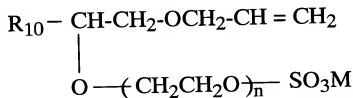
about 30, and M is ammonium.

39. The composition of claim 1 wherein said polymerizable surfactant is a polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salt having the formula:



5 wherein R_{10} is an alkyl group containing 8 to 30 carbon atoms; R_{11} is hydrogen or methyl; A is an unsubstituted or substituted alkylene group having 2 to 4 carbon atoms; n is 0 or an integer of 1 to about 200; and M is an alkali metal, an ammonium ion, or an alkanolamine residue.

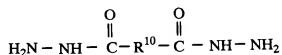
10 40. The composition of claim 39 wherein said polymerizable surfactant is a polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salt having the formula:



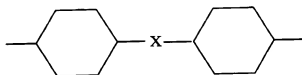
 wherein R_{10} is an alkyl group containing 8 to 14 carbon atoms; and n is an integer of 1 to about 200.

15 41. The composition of claim 1 wherein said polyhydrazide is selected from dihydrazides, trihydrazides, tetrahydrazides, bis-semicarbazides, aromatic polycarboxylic polyhydrazides, or mixtures thereof.

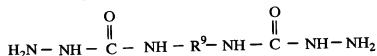
42. The composition of claim 41 wherein said polyhydrazide is selected from dihydrazides represented by the formula



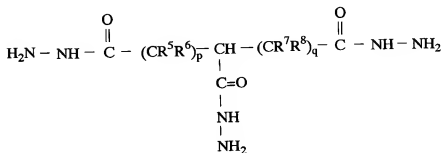
wherein R^{10} is selected from a linear or branched divalent alkylene group having 0 to about 10 carbon atoms, preferably 2 to 10 carbon atoms, a divalent alicyclic group having 4 to about 8 carbon atoms, a divalent aromatic ring, or



wherein the rings are alicyclic or aromatic and X is selected from $-\text{O}-$, $-\text{S}-$, $-\text{SO}_2-$, or $-\text{C}(\text{O})-$; bis-semicarbizides represented by the formula



wherein R^9 is a divalent straight-chain or branched alkylene group having 2 to about 7 carbon atoms or a divalent carbocyclic group having 6 to 8 carbon atoms; trihydrazides represented by the formula



wherein R^5 - R^8 are independently selected from H or OH, p is an integer from 0 to 3, and q is an integer from 2 to 8, provided $p+q \leq 8$ and $p < q$; or mixtures thereof.

43. The composition of claim 42 wherein said polyhydrazide is selected from oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, sebacic acid dihydrazide, maleic acid dihydrazide, fumaric acid dihydrazide, itaconic acid dihydrazide, carbonic acid dihydrazide, phthalic acid dihydrazide, terephthalic acid dihydrazide, isophthalic acid dihydrazide, 1,2,4-butanetricarbohydrazide, 1,1,4-butanetricarbohydrazide, 1,2,5-pentanetricarbohydrazide, 1,3,6-hexane-tricarbohydrazide, 1,3,7-heptanetricarbohydrazide, 1-hydroxy-1,2,4-butanetricarbohydrazide, or mixtures thereof.

44. The composition of claim 41 wherein said polyhydrazide is an aliphatic dicarboxylic acid dihydrazide.

45. The composition of claim 44 wherein said polyhydrazide is adipic acid dihydrazide.

46. The composition of claim 1 further comprising a non-polymerizable surfactant.

47. The composition of claim 46 wherein said non-polymerizable surfactant is an ionic surfactant.

48. The composition of claim 47 wherein said ionic surfactant is an anionic surfactant selected from alkyl aryl sulfonates, alkyl sulfates, sulfates of ethoxylated alcohols, sulfates and sulfonates of ethoxylated alkylphenols, sulfosuccinates, diphenyl sulfonates, or mixtures thereof.

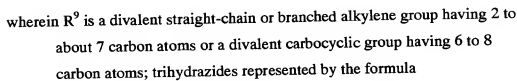
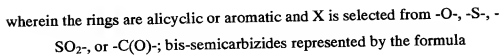
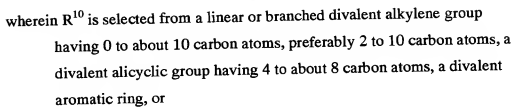
49. A removable, water-whitening resistant pressure sensitive adhesive comprising a crosslinked aqueous emulsion polymer comprising:

(a) about 70 to about 90 wt. % of at least one hydrophobic monomer selected from an alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, or a mixture of at least one styrenic monomer and at least one alkyl (meth)acrylate ester of an alcohol wherein the alkyl portion of the alcohol is linear or branched and contains at least 4 carbon atoms, wherein when a styrenic monomer is present, said

- styrenic monomer is present in an amount up to about 30 wt. % of the total hydrophobic monomer mixture;
- (b) about 2 to about 10 wt. % of at least one hydrophilic monomer;
 - (c) greater than 3 to about 20 wt. % of at least one mono-olefinically unsaturated monomer having an aldehyde or ketone group;
 - (d) 0 to about 45 wt. % of at least one partially hydrophilic monomer selected from alkyl (meth)acrylate esters of an alcohol wherein the alkyl portion of the alcohol has 1 to 2 carbon atoms, N-vinyl-2-pyrrolidone, or mixtures thereof; and
 - (e) about 0.1 to about 5 wt. % of at least one water-soluble or water-dispersible polymerizable surfactant selected from compounds having a terminal allyl amine moiety, substituted phenyl compounds having at least one alkenyl substituent, polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salts, or mixtures thereof;
- wherein said crosslinked aqueous emulsion polymer is crosslinked with at least one polyhydrazide crosslinker, the wt. % of monomers (a), (b), (c) and (d) and the wt. % of polymerizable surfactant (e) are based on the total weight of monomers (a), (b), (c) and (d), and the mean particle size of said crosslinked aqueous emulsion polymer is less than about 400 nm.

50. The composition of claim 49 wherein said polyhydrazide is selected from dihydrazides, trihydrazides, tetrahydrazides, bis-semicarbazides, aromatic polycarboxylic polyhydrazides, or mixtures thereof.

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wherein R^5 - R^8 are independently selected from H or OH, p is an integer from 0 to 3, and q is an integer from 2 to 8, provided $p + q \leq 8$ and $p < q$; or mixtures thereof.

52. The composition of claim 51 wherein said polyhydrazide is selected
5 from oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, sebacic acid dihydrazide, maleic acid dihydrazide, fumaric acid dihydrazide, itaconic acid dihydrazide, carbonic acid dihydrazide, phthalic acid dihydrazide, terephthalic acid dihydrazide, isophthalic acid dihydrazide, 1,2,4-butanetricarbohydrazide, 1,1,4-butanetricarbohydrazide, 1,2,5-
10 pentanetricarbohydrazide, 1,3,6-hexane-tricarbohydrazide, 1,3,7-heptanetri-carbohydrazide, 1-hydroxy-1,2,4-butanetricarbohydrazide, or mixtures thereof.

53. The composition of claim 50 wherein said polyhydrazide is an aliphatic dicarboxylic acid dihydrazide.

54. The composition of claim 53 wherein said polyhydrazide is adipic acid
15 dihydrazide.

55. The composition of claim 49 further comprising a non-polymerizable surfactant.

56. The composition of claim 55 wherein said non-polymerizable surfactant is an ionic surfactant.

- 20 57. The composition of claim 56 wherein said ionic surfactant is an anionic surfactant selected from alkyl aryl sulfonates, alkyl sulfates, sulfates of ethoxylated alcohols, sulfates and sulfonates of ethoxylated alkylphenols, sulfosuccinates, diphenyl sulfonates, or mixtures thereof.

58. A removable, water-whitening resistant pressure sensitive adhesive
25 comprising a crosslinked aqueous emulsion polymer comprising:
(a) about 70 to about 90 wt. % of at least one hydrophobic monomer selected from butyl acrylate, 2-ethylhexyl acrylate, mixtures of butyl acrylate and 2-ethylhexyl acrylate, or a mixture of styrene and at least

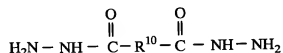
one of butyl acrylate and 2-ethylhexyl acrylate, wherein when styrene is present, said styrene is present in an amount up to about 30 wt. % of the total hydrophobic monomer mixture;

- (b) about 2 to about 10 wt. % of at least one hydrophilic monomer selected from acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, or mixtures thereof;
- (c) about 3.5 to about 20 wt. % of at least one mono-olefinically unsaturated monomer having an aldehyde or ketone group selected from diacetone acrylamide, diacetone acrylate, acrolein, or mixtures thereof;
- (d) 0 to about 25 wt. % of at least one partially hydrophilic monomer selected from methyl acrylate, ethyl acrylate, or mixtures thereof;
- (e) about 0.1 to about 5 wt. % of at least one water-soluble or water-dispersible polymerizable surfactant selected from compounds having a terminal allyl amine moiety, substituted phenyl compounds having at least one alkenyl substituent, polyoxyalkylene-1-(allyloxymethyl) alkyl ether sulfate salts, or mixtures thereof; and
- (f) about 0.1 to about 2 wt. % of at least one non-polymerizable ionic surfactant;

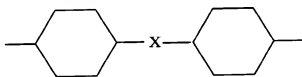
wherein said crosslinked aqueous emulsion polymer is crosslinked with an effective amount of at least one polyhydrazide crosslinker, the wt. % of monomers (a), (b), (c) and (d), the wt. % of polymerizable surfactant (e), and the wt. % of the non-polymerizable surfactant (f) are based on the total weight of monomers (a), (b), (c) and (d), and the mean particle size of said crosslinked aqueous emulsion polymer is less than about 400 nm.

59. The composition of claim 58 wherein said polyhydrazide is selected from dihydrazides, trihydrazides, tetrahydrazides, bis-semicarbazides, aromatic polycarboxylic polyhydrazides, or mixtures thereof.

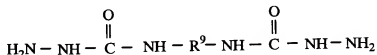
60. The composition of claim 59 wherein said polyhydrazide is selected from dihydrazides represented by the formula



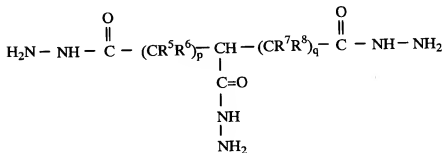
wherein R^{10} is selected from a linear or branched divalent alkylene group having 0 to about 10 carbon atoms, preferably 2 to 10 carbon atoms, a divalent alicyclic group having 4 to about 8 carbon atoms, a divalent aromatic ring, or



wherein the rings are alicyclic or aromatic and X is selected from -O-, -S-, -SO₂-, or -C(O)-; bis-semicarbazides represented by the formula



wherein R^9 is a divalent straight-chain or branched alkylene group having 2 to about 7 carbon atoms or a divalent carbocyclic group having 6 to 8 carbon atoms; trihydrazides represented by the formula



wherein R^5 - R^8 are independently selected from H or OH, p is an integer from 0 to 3, and q is an integer from 2 to 8, provided $p+q \leq 8$ and $p < q$; or

mixtures thereof.

61. The composition of claim 60 wherein said polyhydrazide is selected from oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, sebacic acid dihydrazide, maleic acid dihydrazide, fumaric acid dihydrazide, itaconic acid dihydrazide, carbonic acid dihydrazide, phthalic acid dihydrazide, terephthalic acid dihydrazide, isophthalic acid dihydrazide, 1,2,4-butanetricarbohydrazide, 1,1,4-butanetricarbohydrazide, 1,2,5-pentanetricarbohydrazide, 1,3,6-hexane-tricarbohydrazide, 1,3,7-heptanetricarbohydrazide, 1-hydroxy-1,2,4-butanetricarbohydrazide, or mixtures thereof.
- 10 62. The composition of claim 59 wherein said polyhydrazide is an aliphatic dicarboxylic acid dihydrazide.
63. The composition of claim 62 wherein said polyhydrazide is adipic acid dihydrazide.